Advances in Transport Property Modeling

Methanol (CH_3-OH) is a widely used compound in a broad array of industries including healthcare and energy and yet a comprehensive study of the viscosity of methanol had not been done. This work fills this gap by selecting the most reliable measurements as the basis for a new reference correlation for the viscosity of methanol that is valid over the entire fluid region for vapor, liquid, and supercritical states.

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Methanol (CH_3-OH) is a widely used fluid in the chemical and process industries. It is also an important compound for healthcare as well as medical and pharmaceutical applications. The oldest use of methanol is in the conversion of biomass. This process is gaining importance because it produces a fuel that does not cause a net increase of carbon dioxide in the Earth's atmosphere. Even more prominent is the role of methanol as a hydrogen-rich fuel for electrochemical energy converters such as fuel cells. The development of accurate thermophysical property formulations for methanol will aid engineers involved in process design in these and other fields. In addition, since it is the first member of the homologous series of alkanols, its physical properties will help to characterize the properties of the series as a whole. Methanol is one of the most polar molecules, and its size, shape, and charge distribution determine its macroscopic properties. Although a reference-quality equation of state has been developed for the thermodynamic properties of methanol, a comprehensive study of the viscosity of methanol has not yet been carried out. The NIST approach is to use an advanced residual concept for the correlation where the viscosity is expressed as a function of density and temperature that contains a zero-density limit term, a linear-in-density term and a third virial coefficient for the quadratic density term, besides higher-density terms for the compressed fluid region. The objective of this work is to apply kinetic theory to the dilute gas, Rainwater-Friend theory and the third viscosity virial coefficient for the moderately dense gas, and the Enskog dense hard-sphere theory to obtain a correlation for the viscosity of methanol for the entire fluid state that reproduces the most reliable data sets to within their estimated uncertainties and describes the phenomenological behavior of the viscosity of methanol from the triple point to 630 K at pressures up to 8 GPa.

Literature data sources for the viscosity of methanol were collected to a depth that exceeds all previous compilations. More than 250 references were located and screened for viscosity data, the earliest results having been published in 1861. With this many studies, methanol is after water and ethanol the third most measured liquid in viscometry. The temperatures of all data were converted to the ITS-90 temperature scale and their densities were calculated with an equation of state. Thus, all viscosity data of methanol have been transposed on a common basis to make them comparable. This transposition made it also possible to assess the uncertainty of all data even in the numerous cases where no uncertainty was reported in original accounts.

The extensive body of literature data with the added value of NIST-assigned uncertainties was used to develop a new reference-quality correlation for the viscosity of methanol that is valid over the entire fluid region, including vapor, liquid and metastable phases.

To describe the zero-density viscosity with kinetic theory for polar gases, a new expression for the collision integral of the Stockmayer potential was introduced. The initial density dependence was based on the Rainwater-Friend theory. For the first time, a correlation for the temperature dependence of the third viscosity virial coefficient was developed from experimental data and applied in such a viscosity model. The high-density contribution to the viscosity was based on the Chapman-Enskog theory and includes a new expression for the hard-sphere diameter that is a function of both temperature and density. The resulting correlation is applicable for temperatures from the triple point to 630 K at pressures up to 8 GPa. The estimated uncertainty of the resulting correlation (with a coverage factor of two) varies from 0.6 % in the dilute-gas phase between room temperature and 630 K, to less than 2 % for the liquid phase at pressures up to 30 MPa at temperatures between 273 and 343 K, 3 % for pressures from 30 to 100 MPa, 5 % for the liquid from 100 to 500 MPa, and 10 % between 500 MPa and 4 GPa. At very high pressures, from 4 to 8 GPa, the correlation has an estimated uncertainty of 30 % and can be used to indicate the qualitative behavior of the viscosity of methanol.

Correlations of this type strengthen our knowledge infrastructure of thermophysical properties (disseminated through such standard reference databases as NIST REFPROP) and the worldwide lead of NIST in this area. They also serve the immediate needs of customers. Because of its inclusiveness of the available data, their thorough uncertainty assessment, and the advanced modeling methodology, the correlation is a standard reference benchmark in various aspects. It directs experimenters in the planning of additional viscosity measurements to close

data gaps or reconcile differing results for methanol. It provides also orientation to plan viscosity measurements of other fluids that are chemically similar to methanol. The novel components of the viscosity model are transferable to viscosity correlations for other fluids thus raising the level of viscosity correlation methodology in general.

Future Plans: The ongoing program of integrated modeling and experimental work will continue to focus on both immediate and specific demands for transport property information and on longer-term efforts to improve our predictive capabilities of important industrial fluids.

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Figure 1:
Visualization of the methanol molecule in terms of an isosurface of the electron density with the electrostatic potential indicating the charge distribution and polarity color-mapped onto it. The chosen electron density level of 0.22×10^{-10} $C\cdot m^{-3}$ (0.002 $e^{-}\cdot bohr^{-3}$) represents about 98% of the molecule. The molecule is shown in three orientations to give a better impression of its size, shape, charge distribution, and polar centers.